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(54) Name of Invention: CATALYST FOR REMOVING NITROGEN OXIDE IN EXHAUST GAS

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## SPECIFICATION

### 1. Name of the Invention

Catalyst for Removing Nitrogen Oxide in Exhaust Gas

### 2. Claim

A catalyst for removing nitrogen oxide in exhaust gas, comprising a carrier for the catalyst having solid acid strength of  $pK_a \leq -3.3$  and an active component having formation enthalpy of  $\Delta H_f$  (kcal/gram oxygen atom)  $\geq 80$ .

### 3. Detailed Description of the Invention

#### Field of the Invention

The present invention relates to a catalyst for removing nitrogen oxide contained in an exhaust gas such as boiler exhaust gas by catalytic reduction process utilizing ammonia as a reducing agent wherein the temperature of the exhaust gas is preferably at a high temperature range of 400°C to 700°C.

#### Prior Art

Catalytic reduction process with a catalyst utilizing ammonia as a reducing agent is most widely used in the industry today as the method for removing nitrogen oxide from an exhaust combustion gas such as boiler gas in order to prevent air pollution. This method reacts ammonia with nitrogen oxide in the exhaust gas to reduce them into water and nitrogen in the presence of a catalyst. For the catalyst, an activated titanium oxide having large specific surface is known as a carrier to support active component such as tungstic oxide, vanadium oxide, iron oxide, molybdenum oxide, and tin oxide. Other catalysts using carriers such as aluminum oxide with large specific surface supporting tungstic oxide, vanadium oxide, etc. are also known, but the superiority of titanium oxide for exhaust gas containing sulfur oxide such as combustion gas of heavy oil and coal is prominent in terms of its anti-poisoning property. However, the temperature of the exhaust gas preferable for each of these catalysts is limited within the range of 250°C to 400°C. At a lower temperature of the exhaust gas below 200°C, formation of acidic ammonium sulfate etc. is inevitable, which would cause corrosion of downstream apparatus as well as degradation of the catalyst such as blockade of pores. At a higher temperature of the exhaust gas over 400°C, a reverse reaction to form NO due to oxidization of NH<sub>3</sub> becomes dominant, resulting in serious reduction of denitration capability. At the same time, degradation of the catalyst by the heat is also inevitable in this case.

#### Problems to Be solved by the Invention

The inventors thus investigated thoroughly to solve the above-mentioned problems in using the catalyst, particularly to provide a catalyst preferably usable at the high temperature range of 400°C to 600°C.

#### Means to Solve the Problems

The catalyst according to the present invention uses one of carriers having solid acid strength of pKa <= -3.3, more preferably pKa <= -5.6, which are binary oxides made by various methods as exemplified below.

(1) Mixture of two types of metal oxides

(2) Co-precipitate of two types of metal oxides

(3) A metal oxide impregnated with another type of metal oxide

The carrier is made by baking one of these (1) to (3) at 600°C to 900°C, with or without treatment by heteropolyacid.

Specifically, the carriers include  $TiO_2/WO_3$ ,  $TiO_2/SnO_2$ ,  $TiO_2/Al_2O_3$ ,  $TiO_2/SiO_2$ ,  $SiO_2/Al_2O_3$ ,  $TiO_2/ZrO_2$ ,  $ZrO_2/WO_3$ ,  $Al_2O_3/ZrO_2$ ,  $SiO_2/ZrO_2$ , and  $TiO_2/ZnO$ .

A carrier thus made for the catalyst is used to support a metal oxide having a formation enthalpy of  $\Delta H_f$  (kcal/gram oxygen atom)  $\geq 80$ , preferably  $\geq 100$ , as an active component at a percentile composition by equivalent oxide of 0.1 to 10%. Examples of the metal oxide include  $Na_2O_5$ ,  $Cr_2O_3$ ,  $ZnO$ ,  $CeO_2$ ,  $TaO_5$ ,  $La_2O_3$ , and  $HfO_2$ .

A method to manufacture a catalyst containing the above-mentioned carrier and the active component can be selected from public known methods, and it certainly can include an optional use of commonly used component for the manufacture of a catalyst, such as casting aids, casting reinforcements, inorganic fibers, and organic binders. Strong binding of ammonia to the acid point during the denitration reaction can be expected when the formation enthalpy of the carrier falls within the above range, which would prevent the reverse reaction to form NO due to the oxidization of ammonia at high temperature. Also, an oxidization power at the catalytic site formed by the metal oxide can be properly controlled when the formation enthalpy of the oxide as the active component falls within the above range, which would improve the formation of  $N_2$  and the efficiency of the reaction.

#### Effect of the Invention

As described so far, the present invention can provide a catalyst preferable for an exhaust gas at the high temperature range of 400°C to 600°C by appropriately selecting the solid acid strength of the carrier for the catalyst as well as the formation enthalpy of the metal oxide as the active component.

## EXAMPLES

The present invention is now explained further with reference to examples as well as comparative examples, although these examples are not intended to limit the scope of the present invention.

### Example 1

A solution of titanium tetrachloride ( $TiCl_4$ ) at a concentration of 450 g/l (equivalence by  $TiO_2$ ) in 111 l (50 kg as  $TiO_2$ ) was added with a solution of tin tetrachloride ( $SnCl_4$ ) at a concentration of 100 g/l (equivalence by  $SnO_2$ ) in 500 l (50 kg as  $SnO_2$ ) and mixed. The mixture was then diluted by addition of water to make up a total volume of 1 m<sup>3</sup>. They were heated to 70°C with stirring, and ammonia water was added dropwise until pH became 10.0 in about 1 hour to obtain a coprecipitated hydroxides of  $TiO_2/SnO_2$  having a weight ratio of 50/50. The precipitates were filtered and washed by water, then dried at 100°C for 12 hours. The dried matter thus obtained was suspended in 1 m<sup>3</sup> of 6 N -  $H_2SO_4$  and stirred for about 1 hour. The suspension was then filtered, dehydrated, and baked at 600°C for 3 hours to form  $TiO_2/SnO_2$  binary oxides, which were cooled down and ground by a sample mill to adjust granularity. Into the slurry containing these oxides (at a concentration of 500 g/l), a substrate made of ceramic fiber was immersed, then dried and baked at 500°C for 3 hours after excessive slurry was removed. The carrier component supported by the ceramic fiber substrate was two times by weight of the substrate at this stage. The baked substrate and the carrier were then immersed in a solution of cerium nitrate to impregnate cerium oxide ( $CeO_2$ ) as an active component, which were then dried at 100°C for 12 hours and further baked at 500°C for 3 hours to obtain a catalyst for removing nitrogen oxide. The impregnated  $CeO_2$  was 0.1 % by weight of the carrier.

### Example 2

A catalyst for removing nitrogen oxide was obtained by the same method as Example 1 except that the neutralized dried matter of Example 1 was suspended in 1 m<sup>3</sup> of 2 N -  $H_2SO_4$ .

### Example 3

A catalyst for removing nitrogen oxide was obtained by the same

method as Example 1 except that the neutralized dried matter of Example 1 was suspended in 1 m<sup>3</sup> of 0.2 N - H<sub>2</sub>SO<sub>4</sub>.

#### Example 4

A catalyst for removing nitrogen oxide was obtained by the same method as Example 1 except that the dried hydroxide of Example 1 was suspended and stirred for about 1 hour in 1 m<sup>3</sup> of 200 g/l solution of heteropolyacid (silicotungstic acid - Nippon Inorganic Colour & Chemical Co.).

#### Example 5

A solution of titanium tetrachloride at a concentration of 450 g/l (equivalence by TiO<sub>2</sub>) in 111 kg (50 kg as TiO<sub>2</sub>) was diluted by water to make up a total volume of 1 m<sup>3</sup>, and heated to 70°C with stirring. When this solution was neutralized to pH.6.0 by dropwise addition of ammonia water in about 1.5 hour, a part of the ammonia water was first supplemented with 18.5 kg of ammonium ortho-tungstate (a precursor of AMT) at a concentration of 30.0 % by weight (equivalence by WO<sub>3</sub>) and used, then the remaining ammonium water was used, to obtain a coprecipitate of TiO<sub>2</sub>/WO<sub>3</sub> having a weight ratio of 90/10. The precipitates were then filtered, washed by water and dried at 100°C for 12 hours, and further baked at 750°C for 3 hours to obtain TiO<sub>2</sub>/WO<sub>3</sub> binary oxides. They were cooled down and ground by a sample mill to adjust granularity. In the following steps, the same methods as Example 1 were used to obtain catalyst for removing nitrogen oxide except that CeO<sub>2</sub> concentration was made to 0.2 %.

#### Example 6

A catalyst for removing nitrogen oxide was obtained by the same method as Example 5 except that 41.7 kg of the ammonium ortho-tungstate at the concentration of 30.0 % (equivalence by WO<sub>3</sub>) was used and the TiO<sub>2</sub>/WO<sub>3</sub> weight ratio was made to 80/20.

#### Example 7

A catalyst for removing nitrogen oxide was obtained by the same method as Example 5 except that 71.4 kg of the ammonium ortho-tungstate at the concentration of 30.0 % (equivalence by WO<sub>3</sub>) was used and the TiO<sub>2</sub>/WO<sub>3</sub> weight ratio was made to 70/30.

#### Example 8

A solution of titanium tetrachloride at a concentration of 450 g/l (equivalence by  $TiO_2$ ) in 111 l (50 kg as  $TiO_2$ ) was added with a solution of aluminum chloride ( $AlCl_3$ ) at a concentration of 100 g/l (equivalence by  $Al_2O_3$ ) in 500 l (50 kg as  $Al_2O_3$ ) and mixed. The mixture was then diluted by addition of water to make up a total volume of 1 m<sup>3</sup>. They were heated to 70°C with stirring, and ammonia water was added dropwise until pH became 7.0 in about 1 hour, to obtain a coprecipitated hydroxides of  $TiO_2/Al_2O_3$  having a weight ratio of 50/50. The precipitates were filtered and washed by water, dried at 100°C for 12 hours, and further baked at 800°C for 3 hours to obtain  $TiO_2/Al_2O_3$  binary oxides. They were cooled down and ground by a sample mill to adjust granularity. In the following steps, the same methods as Example 1 were used to obtain catalyst for removing nitrogen oxide except that  $CeO_2$  concentration was made to 5.0 %.

#### Example 9

A catalyst for removing nitrogen oxide was obtained by the same method as Example 8 except that 1170 l of the solution of aluminum chloride (117 kg as  $Al_2O_3$ ) at the concentration of 100 g/l (equivalence by  $Al_2O_3$ ) of Example 8 was used to make up the total volume of 1.5 m<sup>3</sup>, and the  $TiO_2/Al_2O_3$  ratio was made to 30/70.

#### Example 10

A catalyst for removing nitrogen oxide was obtained by the same method as Example 8 except that 56 l of the solution of aluminum chloride (5.6 kg as  $Al_2O_3$ ) at the concentration of 100 g/l (equivalence by  $Al_2O_3$ ) of Example 8 was used, and the  $TiO_2/Al_2O_3$  ratio was made to 90/10.

#### Example 11

A solution of oxyzirconium chloride ( $ZrOCl_2 \cdot 8H_2O$ ) at a concentration of 100 g/l (equivalence by  $ZrO_2$ ) in 500 l (50 kg as  $ZrO_2$ ) was added with water to make up a total volume of 1 m<sup>3</sup>. The solution was then heated to 70°C with stirring, and ammonia water was added dropwise until pH became 7.0 in about 1 hour to obtain zirconium hydroxide. This was then filtered, washed by water, and dried at 100°C for 12 hours. The dried matter thus obtained was added with 25.0 kg of ammonium metatungstate at a concentration of 50 % by weight (equivalence by  $WO_3$ ), mixed by thorough kneading, and dried up. The

mixture was baked at 800°C for 3 hours to obtain binary oxides having ZrO<sub>2</sub>/WO<sub>3</sub> weight ratio of 80/20. In the following steps, the same methods as Example 1 were used to obtain catalyst for removing nitrogen oxide except that CeO<sub>2</sub> concentration was made to 0.2 %.

Example 12

A catalyst for removing nitrogen oxide was obtained by the same method as Example 11 except that 66.7 kg of the ammonium metatungstate at a concentration of 50 % by weight (equivalence by WO<sub>3</sub>) of Example 11 was used, and the ZrO<sub>2</sub>/WO<sub>3</sub> weight ratio was made to 60/40.

Example 13

A catalyst for removing nitrogen oxide was obtained by the same method as Example 5 except that La<sub>2</sub>O<sub>3</sub> was used as the catalytic active component to be impregnated.

Example 14

A catalyst for removing nitrogen oxide was obtained by the same method as Example 5 except that Ta<sub>2</sub>O<sub>5</sub> was used as the catalytic active component to be impregnated.

Example 15

A catalyst for removing nitrogen oxide was obtained by the same method as Example 5 except that Nb<sub>2</sub>O<sub>5</sub> was used as the catalytic active component to be impregnated.

Example 16

A catalyst for removing nitrogen oxide was obtained by the same method as Example 5 except that Cr<sub>2</sub>O<sub>3</sub> was used as the catalytic active component to be impregnated.

Comparative Example 1

A catalyst for removing nitrogen oxide was obtained by the same method as Example 5 except that V<sub>2</sub>O<sub>5</sub> was used as the catalytic active component to be impregnated.

Comparative Example 2

A catalyst for removing nitrogen oxide was obtained by the same method as Example 5 except that MoO<sub>2</sub> was used as the catalytic active component to be impregnated.

Comparative Example 3

A catalyst for removing nitrogen oxide was obtained by the same

method as Example 1 except that the step of treating the neutralized dried matter by H<sub>2</sub>SO<sub>4</sub> was omitted.

Each of the catalyst obtained as above was filled in a reactor and contacted with a mixed gas consisting of nitrogen oxide (200 ppm), ammonia (200 ppm), water vapor (10 v/v%), oxygen (2 v/v%), carbon dioxide (12 v/v%), sulfur dioxide (800 ppm), and nitrogen for the remainder, at a space velocity of 10675 Hr<sup>-1</sup> and a temperature of 400°C to 700°C to remove nitrogen oxides (NOx) from the mixed gas by catalytic reduction. It should be noted that the removal rate for nitrogen oxides is defined by the following formula.

Removal rate for nitrogen oxide = (NOx concentration at catalyst layer inlet - NOx concentration at catalyst layer outlet) / NOx concentration at catalyst layer inlet × 100 (%)

Further, acid strength and acid content in each carrier was measured by the n-butylamine titration method. The measurements were conducted as follows. Approximately one gram of a sample was weighed and put into a stoppered 50 ml Erlenmeyer flask with known weight and dried at 110°C for 2 hours. The dried sample was removed into a desiccator to cool it down and its dry weight was measured. Approximately 10 ml of benzene was added to the sample and suspended thoroughly. 0.1 % solution in benzene of each of indicator reagents shown in Table 1 was added dropwise to the suspension, mixed thoroughly, and let stand overnight. On the next day, 1 ml of n/10n-butylamine was added to the sample, mixed well by shaking, and let stand for 2 hours to observe a change in color. If no change of color as shown in Table 1 was observed, additional 1 ml was added, and the same step was repeated further until the change in color was observed. The results are shown in Table 2.

Table 1

Hammett indicator reagent	Basic color	Acidic color	pKa
m-Paranitrochlorobenzene	None	Yellow	-13.2
p-Nitrotoluene	None	Yellow	-10.4

Anthraquinone	None	Yellow	-10.2
Benzalacetophenone	None	Yellow	-5.6
Dicinnamalacetone	Yellow	Red	-3.0
Crystal Violet	Blue	Yellow	+0.8
p-Dimethylaminoazobenzene	Yellow	Red	+3.3
Methyl Red	Yellow	Red	+4.8
Neutral Red	Yellow	Red	+6.8

Table 2

	pKa of Carrier(<=)	Catalyst -ΔHf of active species (kcal/gram oxygen atom)	Reaction temperature			
			400°C	500°C	600°C	700°C
Example 1	-13.2	116.5	88.2	93.1	95.2	77.7
... 2	-5.6	...	89.9	92.6	92.1	81.5
... 3	-3.0	...	90.2	93.6	88.5	70.1
... 4	-10.4	...	90.1	92.8	94.6	77.2
... 5	-13.2	...	90.6	93.8	95.9	83.3
... 6	-8.3	...	92.1	94.2	94.6	82.5
... 7	-5.3	...	92.1	93.9	90.8	79.5
... 8	-10.4	...	88.8	94.6	96.8	81.1
... 9	-8.3	...	90.2	95.2	95.1	78.5
... 10	-3.0	...	92.3	93.8	90.2	71.0
... 11	-13.2	...	91.1	93.2	96.3	83.0
... 12	-5.3	...	92.1	93.8	93.1	78.8
... 13	-13.2	152.7	90.2	92.2	94.5	83.2
... 14	...	100.0	89.9	93.1	94.8	83.3
... 15	...	92.6	90.9	93.9	94.6	80.2
... 16	...	89.9	91.1	93.1	90.2	71.0
Comparative Example 1	...	74.6	92.0	86.0	55.9	25.3
... 2	...	65.0	93.1	85.8	62.6	36.1
... 3	+3.3	116.5	86.9	59.8	10.2	-30.8